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Contractor's Final Report

on

**Surface Chemistry and Electrochemistry at Electrode-Ionic Liquid Interfaces**

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## Abstract

The overall project goal was to understand and optimize electrode processes in nonflammable ionic liquid electrolytes for application in safe, reliable batteries. For anode development, the nucleation-growth mechanisms and the formation of the solid electrolyte interfaces during lithium and sodium electrodepositions were evaluated. While sodium exhibited classic instantaneous nucleation-growth behavior, lithium electrodeposition consisted of two sequential nucleation-growth steps and was consistent with the substrate electrode surface being heterogeneous towards lithium nucleation. Also, impedance studies confirmed the formation of a solid electrolyte interface at both lithium and sodium electrodeposits; however, the interface at sodium was approximately ten times more resistive than the lithium interface. For cathode development, spin-coated vanadium oxide xerogel films were prepared using sequential casting techniques and were seen, using scanning electron microscopy, to possess a layered structure with thin sheets running parallel to the casting surface. Finally, novel ionic liquid-polymer gel electrolytes, composed of a perfluoroanion ionic liquid and a poly(vinylidene fluoride) hexafluoropropylene, copolymer were developed and characterized during this project. The ionic conductivities of these nonvolatile, nonflammable solid-state electrolytes were measured from room-temperature to 100 °C and found to increase from *ca.* 1 mS cm<sup>-1</sup> to *ca.* 15 mS cm<sup>-1</sup> over this temperature range.

Keywords: electrochemistry, electrodeposition, batteries, ionic liquids, lithium, sodium, vanadium oxide, xerogels, gels, polymer, solid-state electrolytes.

## 1. Introduction

The overall goal of this program was to develop an understanding of the fundamental electrode processes that would allow alkali metal anodes and metal oxide cathodes to be used in chloroaluminate and nonchloroaluminate ionic liquid electrolytes for rechargeable battery systems. The program was subdivided into four individual project objectives, which were the following:

- For lithium and sodium electrodes, identify electrolyte additives (*e.g.*  $\text{SOCl}_2$ ) that produce an ionically conducting solid electrolyte interface (SEI) at the electrode-ionic liquid interface and prevent reaction of the active alkali metal with the ionic liquid electrolyte.
- Evaluate and understand the nucleation and growth process for alkali metal electrodeposition in the presence of the SEI-forming electrolyte additives.
- Produce non-dendritic deposits of lithium and sodium by controlling the nucleation and growth processes with appropriate electrolyte additives or with electrochemical pulse protocols.
- Evaluate and optimize the fundamental electrochemical parameters (*i.e.*, heterogeneous electron transfer kinetics, surface ion injection rates, and solid state ion diffusion coefficients) for vanadium oxide,  $\text{V}_2\text{O}_5$ , xerogels (XRGs) and aerogels (ARGs) using macroelectrode and microelectrode techniques.

The above goals were modified during the course of this project as a result of personnel changes and because the discovery of novel ionic liquid-polymer gel electrolytes led to new, fruitful research direction. These project modifications are summarized in the next two paragraphs.

Due to the departure at the start of the project of co-PI Dr. Andrew L. Tipton, the  $\text{V}_2\text{O}_5$  XRG and ARG portions of the program were delayed. However, spin-coated  $\text{V}_2\text{O}_5$  xerogels were prepared and characterized with scanning electron microscopy by Ms. Amy C. Breda (Staff Scientist from 10/96-12/96) and Dr. Tae H. Cho (Senior Scientist from 3/97-7/97) -- preliminary results of this work are contained in this report. In April 1996, Dr. Joan Fuller was hired as a Senior Scientist, and she became a project co-PI in September 1996. Dr. Fuller took on full responsibility for the lithium and sodium nucleation-growth studies and for the evaluation of the alkali metal solid electrolyte interfaces (SEI) by AC-impedance. Preliminary results of her studies are contained in this report, and full analyses and discussions will appear in future open-literature publications.

During this project, Dr. Fuller and Ms. Breda discovered and developed novel solid-state ionic liquid-polymer gel electrolytes. These versatile electrolytes are composed of an ionic liquid retained in a poly(vinylidene fluoride) hexafluoropropylene copolymer (PVdF(HFP)) matrix and are an extension of earlier work by Dr. Fuller on gels made from ionic liquids and amorphous poly(ethylene oxide) (aPEO) (first Progress Report). The impetus of this work was to develop solid-state electrolytes with the same beneficial properties as the chloroaluminate and nonchloroaluminate ionic liquid electrolytes (*vide infra*) originally proposed as electrolytes for this project. The success of this ionic liquid polymer gel as solid-state electrolytes has already led to one reviewed publication (reference), and more recent results are contained in this report.

## 2. Objectives

During FY97, ionic liquid-polymer gel electrolytes were developed and evaluated. However, due to the termination of this program following this funding period, this aspect of the program was not officially added to the individual project objectives.

## 3. Status of Effort

The program was terminated after the departure of project personnel from Covalent Associates, Inc.

## 4. Accomplishments/New Findings

All materials and experimental procedures are readily available in the open literature<sup>1-11</sup> and so are not described in this report.

### 4.1. Lithium and Sodium Nucleation-Growth in Buffered Neutral Ionic Liquids Containing $\text{SOCl}_2$

Standard chronoamperometry techniques were employed to evaluate the nucleation and growth of lithium and sodium electrodeposition from neutral buffered 1.1:1.0:0.1 and 1.5:1.0:0.5  $\text{AlCl}_3$ :EMIC:MCl (EMIC = 1-ethyl-3-methylimidazolium chloride; MCl = LiCl or NaCl) containing  $\text{SOCl}_2$  at a variety of electrode materials.<sup>10-12</sup> The data was analyzed by comparing normalized chronoamperometric transient theoretical curves for instantaneous and progressive nucleation-growth.<sup>10,12</sup> Data was normalized to the chronoamperometric maximum using  $t/t_m$  and  $(I/I_m)^2$ . Preliminary evaluations of the data are described in this Final Report; however, the data is still be examined and interpreted, and these analyses will appear in future publications.

In all cases, sodium electrodeposition exhibited classic instantaneous nucleation-growth with nucleation site densities fell in the range  $0.5\text{-}1.3 \times 10^6$  sites  $\text{cm}^{-2}$ . This was relatively low compared to values of  $10^6$  to  $10^9$  sites  $\text{cm}^{-2}$  typically found for nucleation site densities<sup>13</sup> and may be indicative of nucleation at a hindered, or partially passivated, electrode surface.

Lithium electrodeposition was more complex. Fig. 1 shows typical normalized chronoamperometric curves for lithium electrodeposition at a Ni disk electrode. At all potentials, the chronoamperometric traces exhibited a short-time maximum that corresponded to a progressive nucleation and growth transient with an overall nucleation site density of  $8.3 \times 10^6$ , ten times higher than the density found for sodium. However, as the chronoamperometric experiments proceeded a second nucleation-growth transient was observed. Because this second transient caused the total current to rise above the diffusion-limited current expected from only the initial nucleation-growth processes, it is postulated that the substrate electrode consists of at least two macroscopic areas exhibiting different nucleation-growth behavior -- one relatively unhindered (short-time transient) at a "clean" surface and the other slowed by a partially passivated surface (long-time transients). Therefore, although the entire surface of the substrate

electrode eventually undergoes nucleation-growth during lithium electrodeposition, the process occurs at different times and with different nucleation parameters (*i.e.* site density and nucleation rate) in various regions of the electrode area. Importantly, the unnormalized currents for the initial transient were well below the Cottrell values expected for an electrode of this size; however, the unnormalized currents for the second, long-time transient were consistent with macroscopic Cottrell behavior over the entire electrode area. These observations are consistent with the postulated mechanism involving heterogeneity of the electrode surface. The heterogeneity of the nucleation-growth process across the electrode may be partially responsible for the dendritic growth observed for lithium.<sup>2</sup>

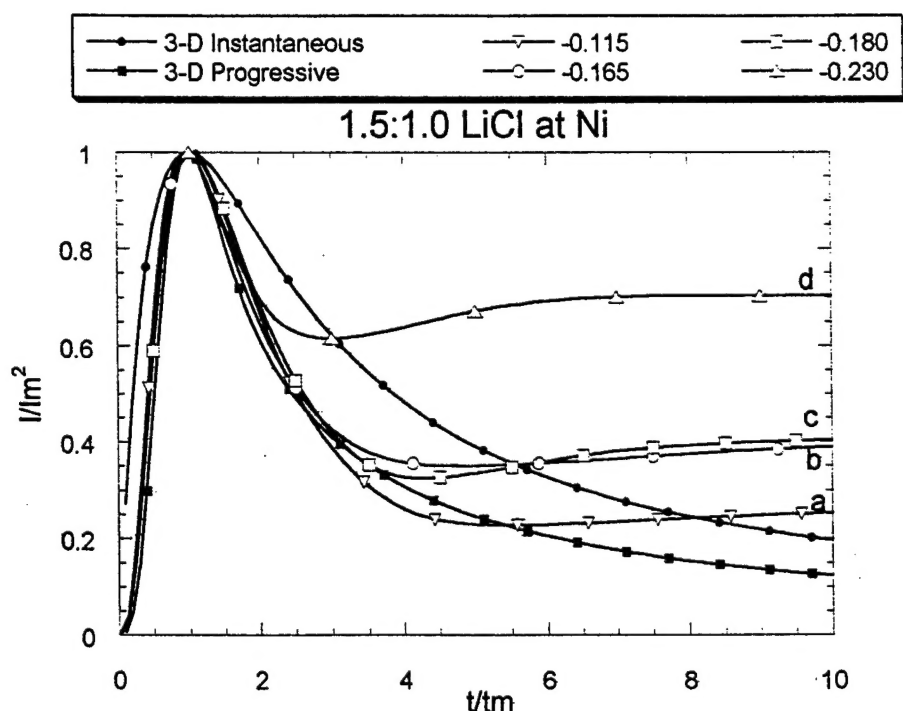


Fig. 1. Normalized chronoamperometric curves for lithium electrodeposition from 1.5:1.0:0.5  $\text{AlCl}_3\text{:EMIC:LiCl}$ . Potentials are referenced to the  $\text{Li/Li}^+$  open-circuit potential and correspond to true overpotentials. Experimental curves are shown as open symbols, while theoretical curves for progressive and instantaneous nucleation are represented by the filled symbols.

#### 4.2. AC-Impedance Studies of Lithium and Sodium Electrodeposits

Lithium and sodium electrodeposits produced from the same melts as in Section 4.1 were examined using AC-impedance. These studies were intended to evaluate the presence, growth, and stability of the solid electrolyte interface (SEI) produced at on the surface of the

electrodeposited alkali metal. As in Section 4.1, preliminary evaluations of the data are described in this Final Report, and more detailed analyses will appear in future publications.

Figures 2 and 3 show Nyquist plots of the AC-impedance data at a tungsten disk electrode for the clean electrode (curve 1), after reduction of  $\text{SOCl}_2$  only (curve 2), and after alkali metal electrodeposition (curves 3-5). Curves 3-5 were collected sequentially and were started after deposition of 0, 15, and 30 min. All data were collected from 1-100,000 Hz. The important results from these two figures were the following: (1) the electrode before and after  $\text{SOCl}_2$  reduction showed simple capacitance behavior; (2) both lithium and sodium exhibited capacitance loops consistent with the presence of an SEI on the alkali metal surface; (3) the resistance of the SEI increased with time for both metals; and (4) based on the capacitance loops at higher frequencies, the sodium SEI possessed a higher resistance (*ca.* ten times greater) and higher capacitance than the lithium SEI. Importantly, these results are the first direct confirmation of SEI formation on the alkali metal surface in these ionic liquid electrolytes.<sup>2,3,7</sup> Also, the latter result is consistent with a thinner (higher capacitance), higher resistive compact SEI for sodium than for lithium and may account for the higher overpotentials observed for sodium electrodeposition and stripping in these electrolytes.<sup>3</sup> The lithium SEI also exhibited a large capacitance loop at low frequencies, indicative of a thick porous layer in series with the compact SEI layer.

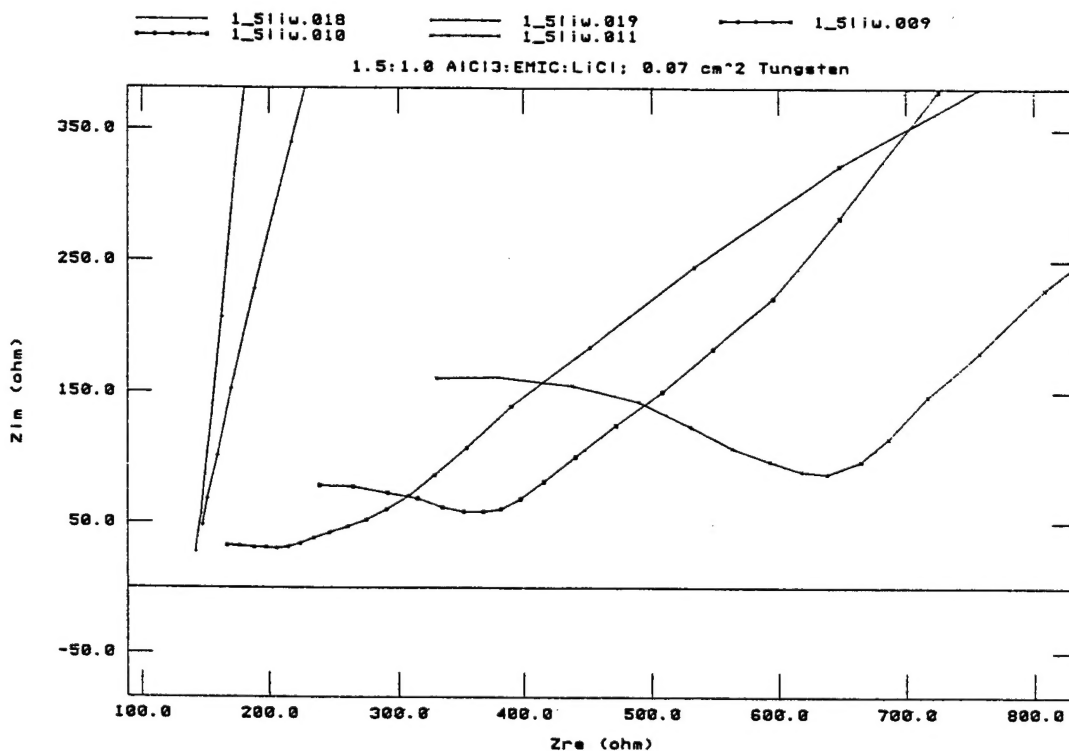


Fig. 2. Nyquist plot of the AC-impedance data for lithium electrodeposited from a 1.5:1.0:0.5  $\text{AlCl}_3$ :EMIC:LiCl ionic liquid.



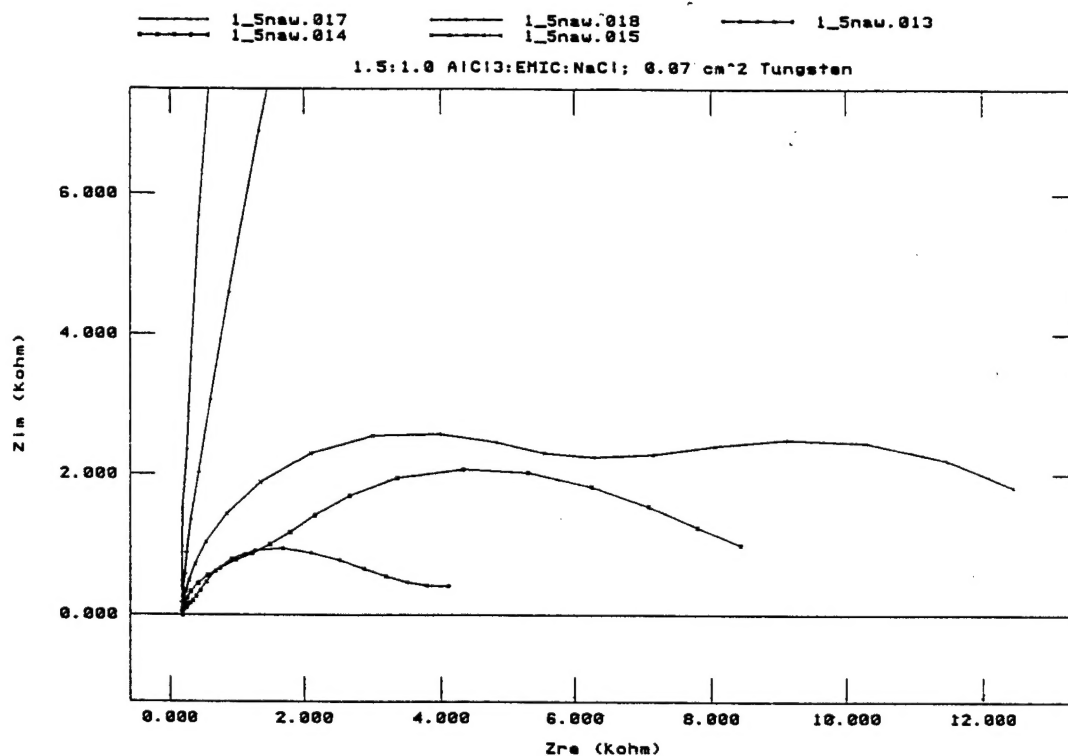


Fig. 3. Nyquist plot of the AC-impedance data for sodium electrodeposited from a 1.5:1.0:0.5 AlCl<sub>3</sub>:EMIC:NaCl ionic liquid.

#### 4.3. SEM Characterization of Lithium and Sodium Electrodeposits

Lithium and sodium electrodeposits were produced on nickel wire and examined with SEM. Unfortunately, limitations of the company EDS attachment precluded quantitative analysis of these samples; instead, the EDS spectra were used only to confirm the presence of sodium, aluminum, nickel, and chloride in the samples -- the EDS could not analyze for lithium.

SEM micrographs for sodium and lithium shown in Fig. 4 and 5, respectively. Although the lithium appeared to be rougher than the sodium, there was little difference in the physical appearance of the electrodeposits. Both deposits exhibited charging effects at various regions of the sample, consistent with the presence of an insulating film of LiCl or NaCl or of partially hydrolyzed melt. In the sodium samples, it was possible to see NaCl crystallites a numerous locations on the sample, consistent with the formation of NaCl on the surface of the sodium metal. However, these results should be viewed with caution until more comprehensive analyses of the alkali metal surface can be performed (*e.g.* XPS and XRD analyses).



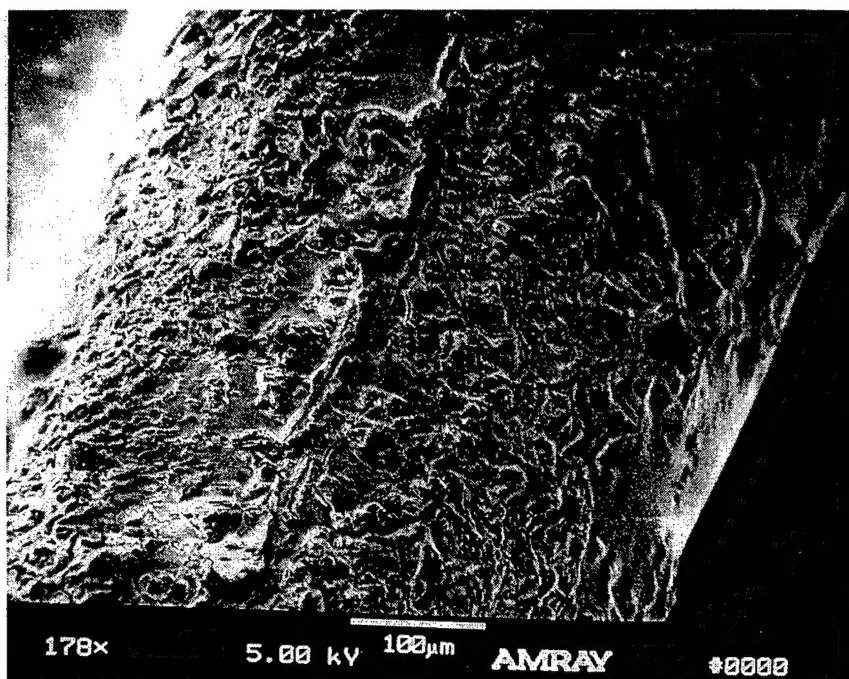


Fig. 4. SEM micrograph of a lithium electrodeposit on Ni wire.

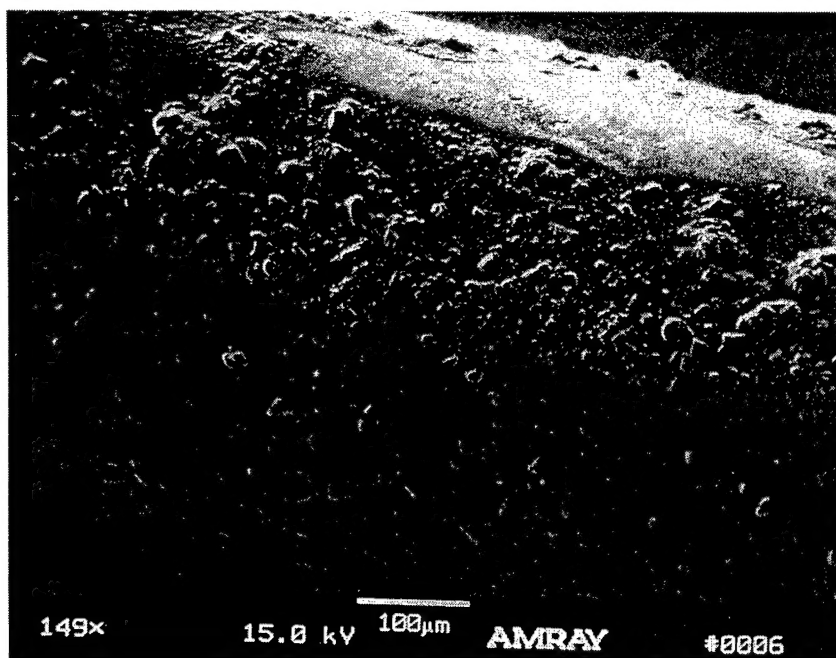


Fig. 5. SEM micrograph of a sodium electrodeposit on Ni wire.

#### 4.4. SEM Characterization of Spin-Coated Vanadium Oxide Xerogels

After much trial and error, spin-coated samples of  $V_2O_5$  xerogels were produced on 1 cm diameter nickel foil. This procedure is clearly an art requiring fine tuning by the operator. To achieve relatively thick samples, the spin-coating procedure was repeated several times for each sample. Surface micrographs of the spin-coated  $V_2O_5$  sample were essentially identical to those reported previously.<sup>14</sup> However, by scratching the surface of the spin-coated film, an edge-on view of the  $V_2O_5$  was possible -- this is shown in Fig. 6. Most striking is the layered structure of the film parallel to the nickel substrate. Such structures have not been reported in the literature and may be a product of the method of film preparation used here, *i.e.* multiple spin-coating steps for each sample.

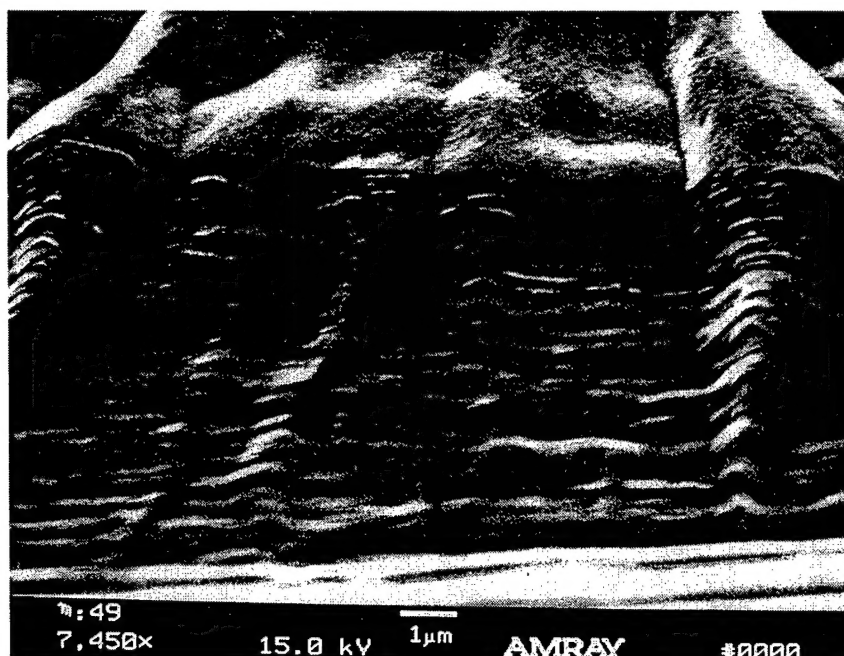


Fig. 6. SEM micrograph of spin-coated  $V_2O_5$  sample on Ni foil.

#### 4.5. Ionic Liquid-Polymer Gel Electrolytes

Novel ionic liquid-polymer gels, composed of a perfluoroanion ionic liquid and a poly(vinylidene fluoride) hexafluoropropylene copolymer (PVdF(HFP)), were evaluated for application as solid-state electrolytes. The preparation of these materials have been thoroughly described in a recent publication<sup>1</sup> and so is not elaborated upon here. Table 1 summarizes the temperature dependent conductivities and activation energies for conductivity ( $E_A$ ) of the ionic liquid-PVdF(HFP) gel electrolytes and of the corresponding neat ionic liquids.

Table 1. Ionic conductivity parameters for ionic liquid-PVdF(HFP) gel electrolytes and corresponding neat ionic liquids.

Ionic Liquid	Mass Ratio <sup>a</sup>	$\kappa/\text{mS cm}^{-1}$ 22 - 23 °C	$\kappa/\text{mS cm}^{-1}$ 100 °C	$E_A/\text{kcal mol}^{-1}$
EMI(triflate)	2:1 (MP)	2.2	22.9	6.6
EMI(triflate)	1:1 (MP)	0.6	9.1	8.0
EMI(triflate)	0.4:1 (MP)	0.06	4.5	8.5
EMIBF <sub>4</sub>	2:1 (PC)	3.2	14.4	5.0
EMIBF <sub>4</sub>	1:1 (PC)	1.4	16.4	6.6
EMIBF <sub>4</sub>	0.5:1 (PC)	0.1	7.3	11.7
BMIPF <sub>6</sub> <sup>c</sup>	2:1 (MP)	0.6	13.7	8.8
BMIPF <sub>6</sub> <sup>c</sup>	1:1 (MP)	0.1	7.3	11.9
EMI(triflate)	neat	9.3 <sup>d</sup>	55.3	4.2
EMIBF <sub>4</sub>	neat	13.8	59.0	4.3
BMIPF <sub>6</sub> <sup>c</sup>	neat	1.8	15.6	6.1

<sup>a</sup>Ionic liquid:PVdF(HFP) mass ratio; <sup>b</sup>Organic solvent used in gel preparation is indicated in parentheses, where MP = 4-methyl-2-pentanone and PC = propylene carbonate; <sup>c</sup>BMI = 1-butyl-3-methylimidazolium; <sup>d</sup>25 °C value from Ref. 8.

From Table 1 several observations can be made: (1) The ionic conductivities of the gels increase as the ionic liquid:PVdF(HFP) mass ratio increases. This also tracks with the physical characteristics of the gels, which progress from a relatively stiff film at the 0.4:1 or 0.5:1 mass ratio to a flexible film at the 2:1 weight ratio. (2) The  $E_A$  values increase with decreasing ionic liquid:PVdF(HFP) mass ratios so that the enhancements in  $\kappa$  with increasing mass ratios are not as dramatic at 100 °C as they are at room temperature. In fact, at 100 °C,  $\kappa$  for 1:1 EMIBF<sub>4</sub>-PVdF(HFP) is actually greater than  $\kappa$  for 2:1 EMIBF<sub>4</sub>-PVdF(HFP), though subtle differences in sample preparation may be partially responsible for this inversion in expected conductivities. (3) The ionic conductivities of the gels track with the ionic conductivities of the corresponding neat ionic liquids. Therefore, neat EMI(triflate) and EMIBF<sub>4</sub> possess similar ionic conductivities as do their gels, while the ionic conductivities for neat BMIPF<sub>6</sub> and its gels are lower than the ionic conductivities for the other ionic liquid-PVdF(HFP) gels having the same ionic liquid:PVdF(HFP) mass ratios.

## 5. Personnel Supported

Dr. Richard T. Carlin (co-P.I., Senior Scientist): Approximately 1/2 time from 31 Oct 96 to 31 Mar 97 and full time from 1 Apr 97 to 31 Jul 97.

Dr. Joan Fuller (co-P.I., Senior Scientist): Full time from 31 Oct 96 to 31 Jul 97.

Dr. Tae H. Cho (Senior Scientist): Full time from 15 Mar 97 to 31 Jul 97.

Ms. Amy C. Breda (Staff Scientist): Approximately 1/2 time from 1 Oct 96 to 1 Nov 96.

Ms. Amy Breda was hired in October of last year to work 1/2 time on this project. Dr. Tae C. Cho transferred to this project during March of this year.

## 6. Publications (Oct 96 to Present)

### Peer Reviewed Publications (Project Personnel Only):

"Ionic Liquid-Polymer Gel Electrolytes," J. Fuller, A. C. Breda, R. T. Carlin, *J. Electrochem. Soc.* **144**, L67 (1997).

"Ionic Liquid-Polymer Gel Catalytic Membrane," R. T. Carlin and J. Fuller, *J.C.S., Chem. Comm.* (in press).

"Reductive Carbonylation of Bis(cyclopentadienyl)titanium Dichloride in a Room-Temperature Chloroaluminate Molten Salt," R. T. Carlin and J. Fuller, *Inorg. Chim. Acta* (in press).

### Collaborative Peer Reviewed Publications:

"Gutmann Acceptor Properties of LiCl, NaCl, and KCl Buffered Ambient-Temperature Chloroaluminate Liquids," R. A. Mantz, P. C. Trulove, R. T. Carlin, and R. A. Osteryoung, *Inorg. Chem.*, **36**, 1227 (1997).

"Electron Transfer Kinetics for Weakly-Bonded, Labile Metal-Ligand Complexes," R. T. Carlin, P. C. Trulove, R. A. Mantz, J. J. O'Dea, and R. A. Osteryoung, *J. C. S., Faraday Trans.*, **92**, 3969 (1996).

"Electrochemistry of Room-Temperature Chloroaluminate Molten Salts at Graphitic and Non-Graphitic Electrodes," R. T. Carlin, J. Fuller, K. Kuhn, M. J. Lysaght, and P. C. Trulove, *J. Applied Electrochem.*, **26**, 1147 (1996).

"The Room-Temperature Ionic Liquid 1-Ethyl-3-Methylimidazolium Tetrafluoroborate: Electrochemical Couples and Physical Properties," J. Fuller, R. T. Carlin, and R. A. Osteryoung, *J. Electrochem. Soc.* (in press).

"Microelectrode Evaluation of Aluminum Alloy Electrodeposition in Chloroaluminate Ionic Liquids," R. T. Carlin, H. C. De Long, J. Fuller, and P. C. Trulove, *J. Electrochem. Soc.* (submitted).

"Magnesium Anodization in Chloride-Rich Room-Temperature Ionic Liquids," J. Fuller, R. T. Carlin, R. A. Osteryoung, and R. A. Mantz, *J. Electrochem. Soc.* (in preparation).

#### Editorial Review:

R. T. Carlin, "Room-Temperature Ionic Liquids: Update from the Tenth International Symposium on Molten Salts," *Molten Salts Bulletin*, No. 61, 1996, p. 3.

#### Proceedings Articles:

J. Fuller and R. T. Carlin, "Anodization of Light Metals in Chloride Rich Room Temperature Ionic Liquids," submitted for the *Proceedings on Electrode Materials and Processes for Energy Conversion and Storage IV* from The Electrochemical Society Spring Meeting, Montreal, Canada, May 1997.

R. T. Carlin, J. Fuller, and A. C. Breda, "Ionic Liquid-Polymer Gel Electrodes," submitted for the *Proceedings on Polymer Electrolytes* from The Electrochemical Society Spring Meeting, Montreal, Canada, May 1997.

R. T. Carlin and J. Fuller, "Room-Temperature Ionic Liquid Battery Electrolytes," *Proceeds of the 12th Annual Battery Conference on Applications and Advances*, January 14-17, 1997, Long Beach, CA.

## **7. Interactions/Transitions**

#### Symposia Organization:

R. T. Carlin, Co-Chair of the Organizing Committee for the Symposium on "Electrochemistry in Unusual Media and Under Unusual Conditions Insertion Compounds and Processes, and Their Applications," to take place at 193th Meeting of The Electrochemical Society in San Diego, March 1998.

#### Presentations:

R. T. Carlin, J. Fuller, and A. C. Breda, "Ionic Liquid-Polymer Gel Electrolytes," The Electrochemical Society, Spring Meeting, Montreal, Canada, May 1997.

J. Fuller and R. T. Carlin, "Anodization of Light Metals in Chloride Rich Room-Temperature Ionic Liquids," The Electrochemical Society, Spring Meeting, Montreal, Canada, May 1997.

R. T. Carlin, "Aluminum Alloys from Room-Temperature Ionic Liquids," Invited talk presented at New England Local Section of the Electrochemistry Society, Feb. 11, 1997.

R. T. Carlin, "A Visionary Perspective of Room Temperature Molten Salts," Invited talk presented at a symposium in honor of Robert A. Osteryoung, North Carolina State University, Raleigh, NC, Jan. 24-25, 1997.

J. Fuller, "Magnesium Anodization in Chloride Rich Room Temperature Molten Salts," Invited poster presented at a symposium in honor of Robert A. Osteryoung, North Carolina State University, Raleigh, NC, Jan. 24-25, 1997.

#### External Laboratory Interactions:

We are continuing to work with researchers at DoD laboratories and with AFOSR-funded researchers in academia. These collaborations have resulted in three joint publications since October 1996 and in several additional articles submitted or in preparation (see above). An external collaborative project with Prof. John Pojman at the University of Southern Mississippi was chosen as an annual AFOSR highlight (see Honors/Awards).

#### Transitions:

None.

### **8. Discoveries/Inventions/Patent Disclosures**

#### Discoveries:

Ionic liquid-polymer gel electrolytes based on PVdF(HFP). These are an extension of J. Fuller's work on other ionic liquid-PEO polymer gels reported in the programs First Annual Progress Report.

#### Patents Issued or Awarded:

"Stabilized Rechargeable Cell in Molten Salt Electrolyte," R. T. Carlin and J. Fuller, U.S. patent 5,552,238, issued September 3, 1996. Research performed for United States Air Force at FJSRL/USAFA.

"Supercapacitor Battery," H. C. De Long and R. T. Carlin, U.S. patent 5,585,999, issued December 17, 1996. Research performed for United States Air Force at FJSRL/USAFA.

"Hydrophobic Ionic Liquids," V. R. Koch, C. Nanjundiah, and R. T. Carlin, US patent awarded in 1997, Covalent Associates proprietary research.

## 9. Honors/Awards

Research on ionic liquid-polymer gel electrolytes (see First Annual Progress Report) was chosen as an AFOSR Annual Highlight. Portions of the highlighted work were performed through a collaborative project established by Dr. J. Fuller with Prof. John Pojman at the University of Southern Mississippi. Dr. Pojman's research group is partially funded by AFOSR and is interested in understanding and controlling frontal polymerization processes. During the frontal polymerization process, density gradients can form at the propagating front and can lead to hydrodynamic and diffusive instabilities. Therefore, Dr. Pojman and Chris Simmons, an undergraduate student, performed experiments on NASA's KC-135 aircraft in order to simulate zero gravity conditions. For these studies, the Southern Mississippi group loaded the polymerization reactor with the monomer, polymer initiator, and ionic and videotaped the dynamics of the frontal polymerization process the zero-g NASA flights.

## 10. References

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